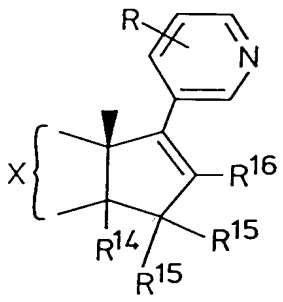
CLAIMS

1. Compounds of the ~~general~~ formula (1)



(1)

wherein X represents the residue of the A, B and C rings of a steroid, R represents a hydrogen atom or an alkyl group of 1-4 carbon atoms, R^{14} represents a hydrogen atom, a halogen atom or an alkyl group of 1 to 4 carbon atoms and each of the R^{15} substituents independently represents a hydrogen atom or an alkyl or alkoxy group of 1-4 carbon atoms, a hydroxy group or an alkylcarbonyloxy group of 2 to 5 carbon atoms or together represent an oxo or methylene group or R^{14} and one of the R^{15} groups together represent a double bond and the other R^{15} group represents a hydrogen atom or an alkyl group of 1 to 4 carbon atoms, and R^{16} represents a hydrogen atom, halogen atom, or an alkyl group of 1 to 4 carbon atoms, in the form of the free bases or pharmaceutically acceptable acid addition salts, but excluding 3β-acetoxy-17-(3-pyridyl)androsta-5,14,16-triene, 3β,15α- and 3β,15β-diacetoxy-17-(3-pyridyl)androsta-5,16-diene and 3β-methoxy-17-(3-pyridyl)-5α-androst-16-ene.

2.Compounds according to Claim 1 wherein X represents the residue selected from the group consisting of

androstan-3α- or 3β-ol,

androst-5-en-3α- or 3β-ol,

androst-4-en-3-one,

androst-2-ene,

androst-4-ene,

androst-5-ene,

androsta-5,7-dien-3α or 3β-ol,

androsta-1,4-dien-3-one,

androsta-3,5-diene,

estra-1,3,5[10]-triene and

estra-1,3,5[10]-trien-3-ol,

each of which, where structurally permissible, can be further derivatised in one or more of the following ways:

- to form 3-esters
- to have one or more carbon to carbon ring double bonds in any of the 5,6-, 6,7-, 7,8-, 9,11- and 11,12-positions
- as 3-oximes
- as 3-methylenes
- as 3-carboxylates
- as 3-nitriles
- as 3-nitros
- as 3-desoxy derivatives
- to have one or more hydroxy, halo, C_{1-4}-alkyl, trifluoro- methyl, C_{1-4}-alkoxy, C_{1-4}-alkanoyloxy, benzoyloxy, oxo, methylene or alkenyl substituents in the A, B or C-ring
- to be 19-nor.

3. Compounds according to Claim 1 which are saturated and unsubstituted at the 11- and 12- positions.

4. 17-(3-Pyridyl)androsta-5,16-dien-3β-ol,

17-(3-pyridyl)androsta-3,5,16-triene,

17-(3-pyridyl)androsta-4,16-dien-3-one,

17-(3-pyridyl)estra-1,3,5[10],16-tetraen-3-ol,

17-(3-pyridyl)-5α-androst-16-en-3α-ol

and their acid addition salts and 3-esters.

5. Compounds according to claim 1 wherein R represents a hydrogen atom.

6. 17-(3-Pyridyl)-5α-androst-16-en-3-one,
17-(3-pyridyl)-androsta-4,16-diene-3,11-dione,
17-(3-pyridyl)-androsta-3,5,16-trien-3-ol,
6α-and 6β-fluoro-17-(3-pyridyl)androsta-4,16-dien-3-one,
17-(3-pyridyl)androsta-4,16-dien-3,6-dione,
3α-trifluoromethyl-17-(3-pyridyl)androst-16-en-3β-ol
and their acid addition salts and 3-esters.

7. 3β-Alkanoyloxy-17-(3-pyridyl)androsta-5,16-dienes in which the alkanoyloxy group has from 2 to 4 carbon atoms.

8. 3β-Acetoxy-17-(3-pyridyl)androsta-5,16-diene.

9. A pharmaceutical composition comprising a compound of Claim 1 in association with a pharmaceutically acceptable carrier or diluent.

10. A pharmaceutical composition comprising a compound of Claim 2 in association with a pharmaceutically acceptable carrier or diluent.

11. A pharmaceutical composition comprising a compound of Claim 3 in association with a pharmaceutically acceptable carrier or diluent.

12. A pharmaceutical composition comprising a compound of Claim 1 wherein R represent a hydrogen atom in association with a pharmaceutically acceptable carrier or diluent.

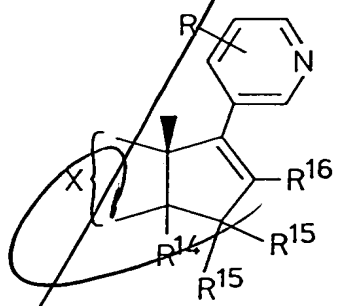
13. A pharmaceutical composition comprising a compound of Claim 4 in association with a pharmaceutically acceptable carrier or diluent.

14. A pharmaceutical composition comprising a compound of Claim 6 in association with a pharmaceutically acceptable carrier or diluent.

15. A pharmaceutical composition comprising a compound of Claim 7 in association with a pharmaceutically acceptable carrier or diluent.

16. A pharmaceutical composition comprising a compound of Claim 8 in association with a pharmaceutically acceptable carrier or diluent.

17. A method of treating an androgen-dependent or estrogen-dependent disorder which comprises administering to a patient in a therapeutically effective dose of a compound of the ~~general~~ formula (1) :



(1)

wherein X represents the residue of the A, B and C rings of a steroid, R represents a hydrogen atom or an alkyl group of 1-4 carbon atoms, R^{14} represents a hydrogen atom, a halogen atom or an alkyl group of 1 to 4 carbon atoms and each of the R^{15} substituents independently represents a hydrogen atom or an alkyl or alkoxy group of 1-4 carbon atoms, a hydroxy group or an alkylcarbonyloxy group of 2 to 5 carbon atoms or together represent an oxo or methylene group or R^{14} and one of the R^{15} groups together represent a double bond and the other R^{15} group represents a hydrogen atom or an alkyl group of 1 to 4 carbon atoms, and R^{16} represents a hydrogen atom, halogen atom, or an alkyl group of 1 to 4 carbon atoms, in the form of a free base or a pharmaceutically acceptable acid addition salt.

18. A method according to Claim 17 wherein the patient has prostatic cancer.

19. A method according to Claim 17 wherein the patient has breast cancer.

20. A method according to Claim 17 wherein X represents a residue selected from the group consisting of

androstan-3α- or 3β-ol,
androst-5-en-3α- or 3β-ol,
androst-4-en-3-one,
androst-2-ene,
androst-4-ene,
androst-5-ene,
androsta-5,7-dien-3α or 3β-ol,
androsta-1,4-dien-3-one,
androsta-3,5-diene,
estra-1,3,5[10]-triene and
estra-1,3,5[10]-trien-3-ol,

each of which, where structurally permissible, can be further derivatised in one or more of the following ways:

- to form 3-esters
- to have one or more carbon to carbon ring double bonds in any of the 5,6-, 6,7-, 7,8-, 9,11- and 11,12-positions
- as 3-oximes
- as 3-methylenes
- as 3-carboxylates
- as 3-nitriles
- as 3-nitros
- as 3-desoxy derivatives
- to have one or more hydroxy, halo, C_{1-4}-alkyl, trifluoro- methyl, C_{1-4}-alkoxy, C_{1-4}-alkanoyloxy, benzoyloxy, oxo, methylene or alkenyl substituents in the A, B or C-ring
- to be 19-nor.

21. A method according to Claim 17 wherein the compound defined in Claim 17 is saturated and unsubstituted at the 11- and 12- positions.

22. A method according to Claim 17 wherein the compound is selected from the group consisting of:

17-(3-pyridyl)androsta-5,16-dien-3β-ol,

17-(3-pyridyl)androsta-3,5,16-triene,

17-(3-pyridyl)androsta-4,16-dien-3-one,

17-(3-pyridyl)estra-1,3,5[10],16-tetraen-3-ol,

17-(3-pyridyl)-5α-androst-16-en-3α-ol

and their acid addition salts and 3-esters.

23. A method according to Claim 17 wherein the compound is a 3β-alkanoyloxy-17-(3-pyridyl)androsta-5,16-diene wherein the alkanoyloxy group has 2 to 4 carbon atoms.

24. A method according to Claim 17 wherein the compound is 3β-acetoxy-17-(3-pyridyl)androsta-5,16-diene.

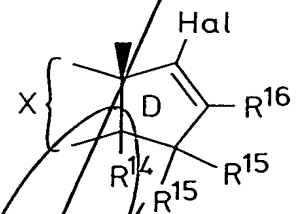
25. An orally ingestible solid composition or a sterile injectable liquid composition comprising respectively a solid or liquid pharmaceutically acceptable carrier or diluent and a compound as defined by general formula (1) of Claim 17.

26. A method of preparing a 3β-hydroxy-or 3β- (lower acyloxy) 16,17-ene-17-(3-pyridyl)-substituted steroid, wherein the 3β-(lower acyloxy) group of the steroid has from 2 to 4 carbon atoms, which comprises subjecting a 3β-hydroxy-16,17-ene-17-iodo or -bromo steroid to a palladium complex-catalysed cross-coupling reaction with a (3-pyridyl)-substituted borane in which the pyridine ring is substituted at the 5-position by an alkyl group of 1 to 4 carbon atoms or is unsubstituted thereat, in a proportion of at least 1.0 equivalent of borane per equivalent of steroid, in an organic liquid which is a solvent for the 3β-hydroxy steroidal reaction product, and, where the 3β-(lower acyloxy) ester is to be prepared, reacting the resulting 3β-hydroxy steroidal reaction product with an esterifying agent effective to replace the hydroxy group by a said lower acyloxy group, which method comprisees (a) carrying out the reaction with 1.0 to 1.2 equivalents of borane per equivalent of steroid or (b) crystallising the product of the cross-coupling reaction from a mixture of

acetonitrile and methanol.

27. A method according to Claim 26, wherein the 3β-hydroxy steroidal reaction product, with or without isolation, is reacted with an acetyl-esterifying agent to give the corresponding 3β-acetoxy-16,17-ene-17-(3-pyridyl) steroid.

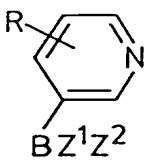
28. A method according to Claim 26, wherein the starting steroid has a D-ring of the following partial formula



wherein Hal is I or Br, X represents the residue of the A, B and C rings of the steroid. R^{14} represents a hydrogen atom, a halogen atom or an alkyl group of 1 to 4 carbon atoms and each of the R^{15} substituents independently represents a hydrogen atom or an alkyl or alkoxy group of 1-4 carbon atoms, a hydroxy group or an alkylcarbonyloxy group of 2 to 5 carbon atoms or together represent an oxo or methylene group or R^{14} and one of the R^{15} groups together represent a double bond and the other R^{15} group represents a hydrogen atom or an alkyl group of 1 to 4 carbon atoms.

29. A method according to Claim 28, wherein the starting steroid is 3β-hydroxyandrost-5-en-17 one.

30. A method according to Claim 28, wherein the (3-pyridyl)-substituted borane is of formula:



wherein R represents a hydrogen atom or an alkyl group of 1-4 carbon atoms and Z^1 and Z^2 independently represent hydroxy or alkoxy or alkyl of 1-3 carbon atoms each or Z^1 and Z^2 together represent an alkylenedioxy group of 2 or 3 carbon atoms.

31. A method according to Claim 26, in which the cross-coupling reaction is carried out in two phases, one of which is aqueous and the other of which comprises the said organic liquid.

32. A method according to Claim 26, feature (b) of claim 26 is employed and the volumetric ratio of acetonitrile to methanol is at least 5:1.

33. A method according to Claim 26, wherein feature (b) of claim 26 is employed and the proportion of borane per equivalent of steroid is from 1.2:1 to 1.5:1.

34. A method according to Claim 26, wherein the ester is prepared and after esterification the product is subjected to reverse phase chromatography.